

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 July 2001 (05.07.2001)

PCT

(10) International Publication Number
WO 01/48080 A1

(51) International Patent Classification⁷: C08L 23/10,
C08K 9/04, C08L 51/06

(21) International Application Number: PCT/US00/34707

(22) International Filing Date:
20 December 2000 (20.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/173,608 29 December 1999 (29.12.1999) US

(71) Applicant (for all designated States except US): THE
DOW CHEMICAL COMPANY [US/US]; 2030 Dow
Center, Midland, MI 48674 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CHOU, Chai-Jing
[US/US]; 1422 Bluestone Drive, Missouri, TX 77459

(US). GARCIA-MEITIN, Eddy, I. [US/US]; 36 Colony
Square, Angleton, TX 77515 (US). SCHILHAB, Lonnie
[US/US]; 213 Bayou Road, Lake Jackson, TX 77566
(US). FIBIGER, Richard, F. [US/US]; 3870 Johns Lane,
Midland, MI 48642 (US).

(74) Agent: ULMER, Duane, C.; The Dow Chemical Com-
pany, Intellectual Property Section, 2301 N. Brazosport
Boulevard, B-1211, Freeport, TX 77541-3257 (US).

(81) Designated States (national): BR, CA, CN, JP, KR, MX,
US.

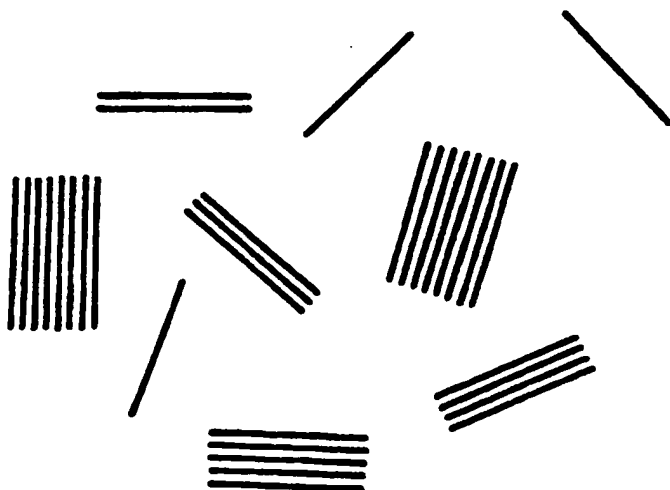
(84) Designated States (regional): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: THERMOPLASTIC OLEFIN NANOCOMPOSITE



(57) Abstract: A polypropylene nanocomposite composition having at least the following two elements. The first element is a maleated polypropylene polymer having a weight average molecular weight greater than 100,000. The second element is a cation exchanging layered silicate material dispersed in the maleated polypropylene so that more than one half of the layers of the cation exchanging layered silicate material are present as one, two, three, four or five layer units upon examination by electron microscopy. A thermoplastic olefin nanocomposite composition can be obtained by interdispersing a thermoplastic elastomer phase with the above-described polypropylene nanocomposite composition.

WO 01/48080 A1

THERMOPLASTIC OLEFIN NANOCOMPOSITE

This application is under a United States
Government contract with The Department of Commerce
5 (NIST)-Advanced Technology Program Project #70NANB7H3028.

BACKGROUND

This invention relates to thermoplastic
polyolefin (TPO) incorporating polypropylene reinforced
10 with delaminated or exfoliated cation-exchanging multi-
layered silicates.

In their natural state, the layers of cation-
exchanging multi-layered silicates, such as
montmorillonite, are held together by ionic bonds to the
15 exchangable cations. As discussed by Kawasumi et al. in
Macromolecules, 1997, 6333-6338, when such silicates are
blended with softened or melted polypropylene, the
resulting shear forces are not sufficient to delaminate or
exfoliate the silicate layers even when the cation is a
20 quaternary ammonium ion because polypropylene is a
relatively non-polar material.

Usuki et al., United States Patent 5,973,053,
solved this problem using two related approaches. The
first approach (also described by Kawasumi et al.) was to
25 blend a quaternary ammonium exchanged multi-layered
silicate with a maleic anhydride modified polypropylene
oligomer and then add an unmodified polypropylene polymer.
The maleic anhydride modified polypropylene oligomer had
sufficient polarity to exfoliate the silicate under the
30 shear conditions of the blending process.

The second approach of Usuki et al. was to blend
a quaternary ammonium exchanged multi-layered silicate

with a maleic anhydride modified polypropylene polymer. The maleic anhydride modified polypropylene polymer had sufficient polarity to exfoliate the silicate under the shear conditions of the blending process.

5 Usuki et al. pointed out that when a maleic anhydride modified polypropylene oligmer was not used, then the average molecular weight of the maleic anhydride modified polypropylene polymer should be limited to about 100,000.

10 Thermoplastic olefin (TPO) is a mechanical blend of a polyolefin (such as polypropylene) and a thermoplastic elastomer (such as EPDM or ultra low density polyethylene). The use of polypropylene based TPO articles at a low temperature is limited because
15 polypropylene based TPO has relatively poor low temperature impact toughness.

SUMMARY OF THE INVENTION

20 The instant invention provides a polypropylene based TPO nanocomposite with a significantly increased low temperature impact toughness. Suprisingly, the key to achieving such toughness is the use of maleated polypropylene polymer having a molecular weight greater than 100,000.

25 More specifically, the instant invention is a thermoplastic olefin nanocomposite composition, comprising: a maleated polypropylene polymer phase having a weight average molecular weight greater than 100,000; a cation exchanging layered silicate material dispersed in
30 the maleated polypropylene phase so that more than one half of the cation exchanging layered silicate material is present as one, two, three, four or five layer units upon

examination by electron microscopy; and a thermoplastic elastomer phase interdispersed with the maleated polypropylene phase.

More generally, the instant invention is a
5 polypropylene nanocomposite composition, comprising: a maleated polypropylene polymer having a weight average molecular weight greater than 100,000; and a cation exchanging layered silicate material dispersed in the maleated polypropylene phase so that more than one half of
10 the cation exchanging layered silicate material is present as one, two, three, four or five layer units upon examination by electron microscopy.

An article of manufacture comprising an object formed of a composition comprising: a maleated polypropylene
15 polymer phase having a weight average molecular weight greater than 100,000; a cation exchanging layered silicate material dispersed in the maleated polypropylene phase so that more than one half of the cation exchanging layered silicate material is present as one, two, three, four or
20 five layer units upon examination by electron microscopy; and a thermoplastic elastomer phase interdispersed with the maleated polypropylene phase.

An article of manufacture comprising an object formed of a composition comprising: a maleated polypropylene
25 polymer having a weight average molecular weight greater than 100,000; and a cation exchanging layered silicate material dispersed in the maleated polypropylene so that more than one half of the cation exchanging layered silicate material is present as one, two, three, four or
30 five layer units upon examination by electron microscopy.

A process for producing a thermoplastic olefin nanocomposite composition, comprising the steps of: mixing a softened or melted polypropylene polymer with an

organic peroxide and maleic anhydride to form a maleated polypropylene polymer; mixing the maleated polypropylene polymer with an onium treated cation exchanging layered silicate material to form a maleated polypropylene nanocomposite; and mixing the maleated polypropylene nanocomposite with a thermoplastic elastomer, the process characterized by the maleated polypropylene having a weight average molecular weight greater than 100,000.

A process for producing a polypropylene nanocomposite composition, comprising the steps of: mixing a softened or melted polypropylene polymer with an organic peroxide and maleic anhydride to form a maleated polypropylene polymer; and mixing the maleated polypropylene polymer with an onium treated cation exchanging layered silicate material to form a maleated polypropylene nanocomposite, the process characterized by the maleated polypropylene having a weight average molecular weight greater than 100,000.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is an idealized drawing made from an electron photomicrographic examination of the maleated polypropylene phase of a TPO composition of the instant invention showing more than one half of the cation exchanging layered silicate material being present as one, two, three, four or five layer units.

DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic olefin (TPO) nanocomposite of the instant invention comprises a maleated polypropylene polymer phase having a weight average molecular weight greater than 100,000, a cation exchanging layered silicate material dispersed in the maleated polypropylene so that

more than one half of the cation exchanging layered silicate material is present as one, two, three, four or five layer units upon examination by electron microscopy (and most preferably, more than one half of the material is so apparent as one, two or three layer units) and a thermoplastic elastomer phase interdispersed with the maleated polypropylene phase. Suprisingly, the weight average molecular weight of the maleated polypropylene polymer can be significantly greater than 100,000, for example, it can be greater than 150,000 or even greater than 250,000.

Referring now to Fig. 1, therein is shown a drawing reproduction of an electron photomicrograph of the maleated polypropylene polymer phase of a TPO composition of the instant invention. The layered silicate material is shown delaminated or exfoliated as: three single layer units, one two layer unit, one three layer unit, one four layer unit, one five layer unit and two eight layer units. A one layer unit typically is a platlet about 1-10 nanometers thick and 100-1000 nanometers wide.

The term "weight average molecular weight" is well known in the instant art and can be determined by, for example, gel permeation chromatography. The term "cation exchanging layered silicate material" is well known in the instant art and includes the "clay mineral" of United States Patent 5,973,053, fully incorporated herein by reference. Examples of cation exchanging layered silicate materials include:

- 1) biophilite, kaolinite, dickalite or talc clays,
- 2) smectite clays,
- 3) vermiculite clays,

- 4) mica,
- 5) brittle mica,
- 6) Magadiite
- 7) Kenyaite,
- 8) Octosilicate,
- 9) Kanemite,
- 10) Makatite, and

11) Zeolitic layered materials such as ITQ-2, MCM-22 precursor, exfoliated ferrierite and exfoliated mordenite.

Many of the above clay materials exist in nature, and also can be synthesized, generally in higher purity than the native material. Any of the naturally occurring or synthetic cation exchanging layered silicate clay materials may be used in the present invention. Preferred are smectite clays, including montmorillonite, bidelite, saponite and hectorite.

An "onium treated cation exchanging layered silicate material" is a cation exchanging layered silicate material that has been exposed to onium cations (usually organic quaternary ammonium compounds) so that the original cation of the cation exchanging layered silicate material is exchanged, at least in part, for the onium cations.

Onium treated cation exchanging layered silicate materials are well known in the instant art, for example, see the above mentioned United States Patent 5,973,053. Onium treated cation exchanging layered silicate materials are commercially available from, for example, Southern Clay Company in the United States.

The term "maleated polypropylene" means a polypropylene containing more than one tenth of one

percent of maleic anhydride grafted to the polypropylene. Maleated polypropylene is commercially available from several sources. Polymer synthesis may be the best way to tailor the molecular weight, molecular weight distribution and the extent of maleic anhydride grafting to the polymer. Solid state maleation in a solution at a temperature below the melting temperature of the polypropylene is another way of preparing maleated polypropylene. Alternatively, as is well known in the instant art, maleated polypropylene can be made by mixing softened or melted unmodified polypropylene with maleic anhydride and an organic peroxide.

Preferably, the weight percent of maleic anhydride of the maleated polypropylene is in the range of from two tenths of one percent to ten percent. Most preferably, the weight percent of maleic anhydride of the maleated polypropylene is in the range of from one half of one percent to two percent.

The amount of cation exchanging layered silicate material used can range from one to fifty percent by weight of the composition. Preferably, the amount of cation exchanging layered silicate material used ranges from three to twelve percent by weight of the composition. The polypropylene nanocomposite composition of the instant invention is obtained when the above discussed thermoplastic elastomer is not used.

The TPO nanocomposite or polypropylene nanocomposite of the instant invention can also contain conventional macro sized fillers such as a carbonate, glass fibers, kaolin, talc, glass beads, graphite fibers and carbon black. The maleated polypropylene of the instant invention can be high crystallinity maleated polypropylene. The term "high crystallinity" is defined

herein as material which has a heat of melting of the maleated polypropylene crystallites of more than 85 Joules per gram of amorphous and crystalline phases of the polymer using the determination outlined on pages 448-494 of Volume 4 of the Encyclopedia of Polymer Science and Engineering, 2nd Edition, 1986, John Wiley & Sons.

The TPO nanocomposite or polypropylene nanocomposite of the instant invention can also comprise non-maleated polypropylene having a weight average molecular weight greater than 100,000. Preferably, the TPO nanocomposite or polypropylene nanocomposite of the instant invention is essentially free of maleated polypropylene oligomer, that is, the concentration of maleated polypropylene oligomer is less than five percent of the total amount of polypropylene. The term "oligomer" herein means a polymer having a molecular weight of less than one thousand. The non-maleated polypropylene can be any type of polypropylene, for example, block co-polymers of polypropylene and ethylene.

The TPO nanocomposite of the instant invention can be made by mixing a heat softened or melted polypropylene polymer of sufficiently high molecular weight with an organic peroxide and maleic anhydride to form a maleated polypropylene polymer which can then mixed with an onium treated cation exchanging layered silicate material and a thermoplastic elastomer.

Another way of making the TPO nanocomposite of the instant invention is to mix a heat softened or melted polypropylene polymer of sufficiently high molecular weight with an organic peroxide and maleic anhydride to form a maleated polypropylene polymer; then mix the maleated polypropylene polymer with an onium treated

cation exchanging layered silicate material and then to mix in the thermoplastic elastomer.

Similarly, the polypropylene nanocomposite of the instant invention can be made by mixing a heat softened or melted polypropylene polymer of sufficiently high
5 molecular weight with an organic peroxide and maleic anhydride to form a maleated polypropylene polymer which can then mixed with an onium treated cation exchanging layered silicate material.

10 The TPO nanocomposite or polypropylene nanocomposite of the instant invention can be used, for example, to make articles of manufacture such as parts for motor vehicles, appliances, business machines or construction articles.

15 COMPARATIVE EXAMPLE

Fifty seven parts by weight of maleated polypropylene having a weight average molecular weight of 50,000 (PP EPOLENE G3003 brand maleated polypropylene from Eastern Chemical Company), thirty three parts by weight of
20 thermoplastic elastomer (AFFINITY 8180 brand low density polyethylene from Dow) and ten parts by weight onium treated cation exchanging layered silicate material (montmorillonite treated with dimethyl, dihydrogenated tallow quaternary ammonium compound from Southern Clay)
25 are mixed in a BANBURY brand polymer mixer at 100 rpm and a temperature of 150 degrees Celsius for ten minutes to produce a thermoplastic olefin nanocomposite having a flex modulus of 207,000 pounds per square inch and a notched IZOD impact strength at 30 degrees below zero Centigrade
30 of 1 foot pound per inch.

EXAMPLE 1

Fifty seven parts by weight of maleated polypropylene having a weight average molecular weight of 150,000 (laboratory prepared by mixing ninety five parts high
5 molecular weight polypropylene with three parts of maleic anhydride and six tenths part di-cumyl peroxide in a BANBURY brand polymer mixer at 200 rpm and 180-200 degrees Celsius for three minutes), thirty three parts by weight of thermoplastic elastomer (AFFINITY 8180 brand low
10 density polyethylene from Dow) and ten parts by weight onium treated cation exchanging layered silicate material (montmorillonite treated with dimethyl, dihydrogenated tallow quaternary ammonium compound from Southern Clay) are mixed in a BANBURY brand polymer mixer at 100 rpm and
15 a temperature of 150 degrees Celsius for ten minutes to produce a thermoplastic olefin nanocomposite having a flex modulus of 183,000 pounds per square inch and a notched IZOD impact strength at 30 degrees below zero Centigrade of 11.6 foot pound per inch. This example shows the
20 substantial increase in impact strength of a thermoplastic olefin nanocomposite of the instant invention relative to the thermoplastic olefin nanocomposite of the COMPARATIVE EXAMPLE.

25 EXAMPLE 2

Thirty parts by weight of maleated polypropylene having a weight average molecular weight of 200,000, twenty seven parts by weight of non-maleated polypropylene having a weight average molecular weight of 150,000,
30 thirty three parts by weight of thermoplastic elastomer (AFFINITY 8180 brand low density polyethylene from Dow) and ten parts by weight onium treated cation exchanging layered silicate material (montmorillonite treated with

dimethyl, dihydrogenated tallow quaternary ammonium compound from Southern Clay) are mixed in a HAAKE brand polymer mixer at 200 rpm and a temperature of 180 degrees Celsius for ten minutes to produce a thermoplastic olefin nanocomposite. Electron microscopy examination of the polypropylene phase of the thermoplastic olefin nanocomposite shows that more than one half of the onium treated cation exchanging layered silicate material is apparent as single, double or triple layer units.

10

EXAMPLE 3

Twenty three parts by weight of maleated polypropylene having a weight average molecular weight of 150,000, forty two parts by weight of non-maleated high crystallinity polypropylene having a weight average molecular weight of 150,000, twenty five parts by weight of thermoplastic elastomer (AFFINITY 8180 brand low density polyethylene from Dow) and ten parts by weight onium treated cation exchanging layered silicate material (montmorillonite treated with dimethyl, dihydrogenated tallow quaternary ammonium compound from Southern Clay) are mixed in a BANBURY brand polymer mixer at 100 rpm and a temperature of 150 degrees Celsius for ten minutes to produce a thermoplastic olefin nanocomposite having a flex modulus of 184,000 pounds per square inch and a notched IZOD impact strength at zero degrees Celsius of 13.7 foot pound per inch. Electron microscopy examination of the polyethylene phase of the thermoplastic olefin nanocomposite shows that more than one half of the onium treated cation exchanging layered silicate material is apparent as single, double or triple layer units.

EXAMPLE 4

Twenty three parts by weight of maleated polypropylene having a weight average molecular weight of 150,000, forty two parts by weight of non-maleated high crystallinity polypropylene having a weight average molecular weight of 150,000, twenty five parts by weight of thermoplastic elastomer (AFFINITY 8180 brand low density polyethylene from Dow), five parts by weight of talc and ten parts by weight onium treated cation exchanging layered silicate material (montmorillonite treated with dimethyl, dihydrogenated tallow quaternary ammonium compound from Southern Clay) are mixed in a BANBURY brand polymer mixer at 100 rpm at a temperature of 150 degrees Celsius for ten minutes to produce a thermoplastic olefin nanocomposite having a flex modulus of 201,000 pounds per square inch and a notched IZOD impact strength at zero degrees Celsius of 12.7 foot pound per inch. Electron microscopy examination of the polyethylene phase of the thermoplastic olefin nanocomposite shows that more than one half of the onium treated cation exchanging layered silicate material is observed as single, double or triple layer units.

EXAMPLE 5

Ninety parts by weight of maleated polypropylene having a weight average molecular weight of 200,000, ten parts by weight of onium treated cation exchanging layered silicate material (montmorillonite treated with dimethyl, dihydrogenated tallow quaternary ammonium compound from Southern Clay) and two tenths part by weight of IRGONOX B225 brand antioxidant are mixed in a HAAKE brand polymer mixer at 200 rpm and a temperature of 180 degrees Celsius for ten minutes to produce a polypropylene nanocomposite.

Electron microscopy examination of the polypropylene nanocomposite shows that more than one half of the onium treated cation exchanging layered silicate material is present as single, double or triple layer units.

5

WHAT IS CLAIMED IS:

1. A thermoplastic olefin nanocomposite composition, comprising:
 - 5 (a) a maleated polypropylene polymer phase having a weight average molecular weight greater than 100,000;
 - (b) a cation exchanging layered silicate material dispersed in the maleated
10 polypropylene phase so that more than one half of the cation exchanging layered silicate material is present as one, two, three, four or five layer units upon examination by electron microscopy; and
 - 15 (c) a thermoplastic elastomer phase interdispersed with the maleated polypropylene phase.
2. The composition of Claim 1, wherein the
20 weight percent of the cation exchanging layered silicate material in the composition is more than one percent and less than thirty percent.
3. The composition of Claim 1, wherein the
25 weight percent of the cation exchanging layered silicate material in the composition is more than three percent of the composition and less than twelve percent of the composition.
4. The composition of Claims 1, 2 or 3,
30 wherein the weight average molecular weight of the maleated polypropylene polymer is greater than 125,000.

5. The composition of Claims 1, 2 or 3,
wherein the weight average molecular weight
of the maleated polypropylene polymer is
greater than 150,000.
- 5 6. The composition of Claims 1, 2 or 3,
wherein the weight average molecular weight
of the maleated polypropylene polymer is
greater than 250,000.
- 10 7. The composition of Claims 1-6, wherein the
maleated polypropylene polymer is high
crystallinity maleated polypropylene,
wherein the heat of melting of the
crystallites of the maleated polypropylene
polymer is greater than 85 Joules per gram.
- 15 8. The composition of Claims 1-7, further
comprising non-maleated polypropylene in
the maleated polypropylene polymer phase,
the non-maleated polypropylene having a
weight average molecular weight greater
20 than 100,000.
- 25 9. The composition of Claim 8, wherein the
non-maleated polypropylene is high
crystallinity non-maleated polypropylene,
wherein the heat of melting of the non-
maleated polypropylene crystallites is
greater than 85 Joules per gram.
- 30 10. The composition of Claims 1-9, wherein the
maleated polypropylene polymer phase is
essentially free of a maleated
polypropylene oligomer.
11. The composition of Claims 1-10, wherein the
impact toughness at zero degrees Celsius by

the notched IZOD test of the composition is increased by more than fifty percent in comparison to a composition being the same except that the weight average molecular weight of the maleated polypropylene is less than 100,000.

12. The composition of Claims 1-11, further comprising talc or other conventional filler material.

13. A polypropylene nanocomposite composition, comprising:

(d) maleated polypropylene polymer having a weight average molecular weight greater than 100,000;

(e) a cation exchanging layered silicate material dispersed in the maleated polypropylene so that more than one half of the cation exchanging layered silicate material is present as one, two, three, four or five layer units upon examination by electron microscopy.

14. The composition of Claim 13, wherein the weight percent of the cation exchanging layered silicate material in the composition is more than one percent and less than thirty percent.

15. The composition of Claim 13, wherein the weight percent of the cation exchanging layered silicate material in the composition is more than three percent of the composition and less than twelve percent of the composition.

16. The composition of Claims 13, 14 or 15,
wherein the weight average molecular weight
of the maleated polypropylene polymer is
greater than 125,000.
- 5 17. The composition of Claims 13, 14 or 15,
wherein the weight average molecular weight
of the maleated polypropylene polymer is
greater than 150,000.
- 10 18. The composition of Claims 13, 14 or 15,
wherein the weight average molecular weight
of the maleated polypropylene polymer is
greater than 250,000.
- 15 19. The composition of Claims 13-18, wherein
the maleated polypropylene polymer is high
crystallinity maleated polypropylene,
wherein the heat of melting of the
crystallites of the maleated polypropylene
polymer is greater than 85 Joules per gram.
- 20 20. The composition of Claims 13-19, further
comprising non-maleated polypropylene in
the maleated polypropylene polymer, the
non-maleated polypropylene having a weight
average molecular weight greater than
100,000.
- 25 21. The composition of Claim 20, wherein the
non-maleated polypropylene is high
crystallinity non-maleated polypropylene,
wherein the heat of melting of the non-
maleated polypropylene crystallites is
30 greater than 85 Joules per gram.
22. The composition of Claims 13-21, wherein
the maleated polypropylene polymer phase is

essentially free of a maleated
polypropylene oligomer.

5 23. The composition of Claims 13-22, wherein
the impact toughness at zero degrees
Celsius by the notched IZOD test of the
composition is increased by more than fifty
percent in comparison to a composition
being the same except that the weight
average molecular weight of the maleated
10 polypropylene is less than 100,000.

24. The composition of Claims 13-23, further
comprising talc or other conventional
filler material.

15 25. An article of manufacture, comprising: an
object formed of the composition of Claims
1-24.

26. The article of manufacture of Claim 25,
wherein the object is a motor vehicle part.

20 27. A process for producing a thermoplastic
olefin nanocomposite composition,
comprising the steps of:

25 (a) mixing a softened or melted
polypropylene polymer with an organic
peroxide and maleic anhydride to form
a maleated polypropylene polymer;

30 (b) mixing the maleated polypropylene
polymer with an onium treated cation
exchanging layered silicate material
to form a maleated polypropylene
nanocomposite; and

(c) mixing the maleated polypropylene
nanocomposite with a thermoplastic

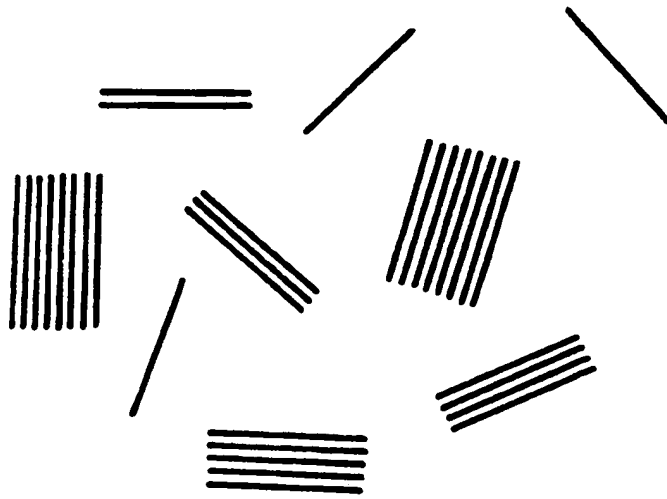
elastomer, the process characterized by the maleated polypropylene having a weight average molecular weight greater than 100,000.

5 28. A process for producing a polypropylene nanocomposite composition, comprising the steps of:

10 (a) mixing a softened or melted polypropylene polymer with an organic peroxide and maleic anhydride to form a maleated polypropylene polymer; and

15 (b) mixing the maleated polypropylene polymer with an onium treated cation exchanging layered silicate material to form a maleated polypropylene nanocomposite, the process characterized by the maleated polypropylene having a weight average molecular weight greater than 100,000.

FIG. 1



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/34707

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L23/10 C08K9/04 C08L51/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 910 523 A (HUDSON STEVEN DAVID) 8 June 1999 (1999-06-08) the whole document	1-28
A	KUROKAWA Y ET AL: "STRUCTURE AND PROPERTIES OF A MONTMORILLONITE/POLYPROPYLENE NANOCOMPOSITE" JOURNAL OF MATERIALS SCIENCE LETTERS, GB, CHAPMAN AND HALL LTD. LONDON, vol. 16, no. 20, 15 October 1997 (1997-10-15), pages 1670-1672, XP000784261 ISSN: 0261-8028 the whole document	1-28



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

20 March 2001

Date of mailing of the international search report

05/04/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bergmans, K

INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 00/34707

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 891 399 A (OHKAWA HIDEO ET AL) 2 January 1990 (1990-01-02) abstract; claims 1-25 column 3, line 30	1-28
P,A	--- ALEXANDRE M ET AL: "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials" MATERIALS SCIENCE AND ENGINEERING R: REPORTS,CH,ELSEVIER SEQUOIA S.A., LAUSANNE, vol. 28, no. 1-2, June 2000 (2000-06), pages 1-63, XP004205143 ISSN: 0927-796X abstract page 33, paragraph 3.3.1.4 table 14	1-28
P,A	--- WO 00 47657 A (FIBIGER RICHARD F ;BARGER MARK A (US); SUH KYUNG W (US); TUNG HARV) 17 August 2000 (2000-08-17) abstract; examples 2,3 -----	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/34707

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5910523 A	08-06-1999	NONE	
US 4891399 A	02-01-1990	JP 1004655 A	09-01-1989
		JP 2043233 C	09-04-1996
		JP 7064983 B	12-07-1995
		JP 1011163 A	13-01-1989
		JP 7064984 B	12-07-1995
		EP 0265839 A	04-05-1988
		JP 63225657 A	20-09-1988
		KR 9108563 B	19-10-1991
WO 0047657 A	17-08-2000	AU 3489800 A	29-08-2000